

First-Order Relativistic Corrections to MP2 Energy from Standard Gradient Codes: Comparison with Results from Density Functional Theory

ROBERT FRANKE, CHRISTOPH VAN WÜLLEN

Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

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ABSTRACT: The evaluation of the first-order scalar relativistic corrections to MP2 energy based on either direct perturbation theory or the mass-velocity and Darwin terms is discussed. In a basis set of Lévy-Leblond spinors the one- and two-electron matrix elements of the relativistic Hamiltonian can be decomposed into a nonrelativistic part and a relativistic perturbation. Thus, a program capable of calculating nonrelativistic energy gradients can be used to calculate the cross-term between relativity and correlation. The method has been applied to selected closed-shell atoms (He, Be, Ne, and Ar) and molecules (CuH, AgH, and AuH). The calculated equilibrium distances and harmonic frequencies were compared with results from first-order relativistic density functional calculations. It was found that the cross-term is not the origin of the nonadditivity of relativistic and correlation effects. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 1596–1603, 1998

Keywords: direct perturbation theory; MP2 gradients; density functional theory; relativistic effects; nonadditivity of relativity and correlation

Introduction

Solving the Dirac–Hartree–Fock problem is the initial step in relativistic calculations for many-electron systems. Standard methods to rem-

edy deficiencies of the one-electron approximation connected to the so-called “dynamic” correlation effect are the configuration interaction (CI) approach, many-body perturbation theory (MBPT) techniques, and, most promising, the coupled cluster (CC) methods. In general, these methods are essentially the same as in the case of nonrelativistic theory. Fully relativistic four-component calculations at the CI level¹ as well as at the MBPT

Correspondence to: R. Franke

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level² have been developed for molecules. A fully relativistic Fock-space CCSD method for atoms has been implemented and applied to closed- and open-shell atoms.³ The major difference from a nonrelativistic treatment (from a computational point of view) is that the relativistic functions are complex four-component spinors. Thus, in spite of symmetries between integrals, fully relativistic calculations are far more time-consuming than their nonrelativistic counterparts. To handle molecular systems with heavy atoms and a large number of electrons, which is already a serious task in nonrelativistic calculations, much effort has been spent on developing methods that can be considered as approximations to the complete relativistic treatment. The most widely used approach is based on the relativistic effective core potentials (RECPs) (see, e.g., ref. 4). The one-electron mass-velocity Darwin (MVD) term has been used to calculate a variety of molecular properties including relativistic correlation contributions up to MBPT(4) (see, e.g., ref. 5). To take higher order contributions to relativistic corrections into account, methods based on the Douglas-Kroll-Hess approach,⁶ the ZORA/CPD scheme,⁷⁻⁹ and direct perturbation theory (DPT)¹⁰⁻¹² have been developed. Recently, Klopper gave a simple recipe for the calculation of the scalar first-order relativistic corrections in the framework of DPT.¹³ It will be shown that this recipe follows from a representation of the one- and two-electron matrix elements of the Dirac-Coulomb operator in a basis of Lévy-Leblond spinors. Calculations based on an implementation of this scheme into a nonrelativistic MP2 energy gradient code for selected closed-shell atoms and molecules are reported and compared with data from the literature. In addition, for molecular systems, we carried out first-order relativistic density functional (DFT) calculations for comparison.

Method

The key idea of DPT is the different handling of positronic and electronic eigenstates of the Dirac equation. For the latter, a transformation in four-component spinor space is applied to the Dirac equation, which replaces the bispinor $\Psi = (\varphi, \chi)$

$$\Psi = \begin{pmatrix} \varphi \\ \chi \end{pmatrix} \rightarrow \tilde{\Psi} = \begin{pmatrix} \varphi \\ \tilde{\chi} \end{pmatrix} = \begin{pmatrix} \varphi \\ c\chi \end{pmatrix} \quad (1)$$

where c is the velocity of light in atomic units, φ the so-called "large component," and χ the "small component." This transformation changes the metric from 1 to

$$\hat{S} = \begin{pmatrix} 1 & 0 \\ 0 & c^{-2} \end{pmatrix} \quad (2)$$

and the one-electron Dirac operator, \hat{D} , after subtracting the rest mass, to

$$\hat{D} = \begin{pmatrix} \hat{V} & \vec{\sigma} \vec{p} \\ \vec{\sigma} \vec{p} & -2 + \frac{1}{c^2} \cdot \hat{V} \end{pmatrix} \quad (3)$$

where \hat{V} is the nuclear potential operator, \vec{p} is the momentum operator, and $\vec{\sigma}$ the vector of the three Pauli matrices ($\sigma_x, \sigma_y, \sigma_z$). From the second line of the one-electron Dirac equation in modified metric

$$\hat{D}\Psi = E\hat{S}\Psi \quad (4)$$

a relation is obtained between the small and large component

$$\chi = \frac{\vec{\sigma} \vec{p} \varphi}{2 - \frac{1}{c^2}(\hat{V} - E)} = \frac{1}{2} \vec{\sigma} \vec{p} \varphi + O(c^{-2}) \quad (5)$$

A special choice of four-component single-particle basis functions, the Lévy-Leblond spinors, shall now be considered

$$\Psi' \equiv \begin{pmatrix} \varphi' \\ \chi' \end{pmatrix} = \begin{pmatrix} \phi \\ \frac{1}{2} \vec{\sigma} \vec{p} \phi \end{pmatrix} \quad (6)$$

where ϕ is a two-component spinor, $g \cdot \eta$, consisting of the spatial function g and a spin function η . Functions according to eq. (6) are solutions of the Lévy-Leblond equation,¹⁴ a linear nonrelativistic wave equation for spin 1/2 particles. This equation is the limit $c \rightarrow \infty$ of the Dirac equation with c -dependent metric (4) for electronic states.¹¹ Functions of the form defined by eq. (6) limit the domain of the Lévy-Leblond operator, which then becomes bounded from below.¹¹ In expanding the large component φ of the Dirac spinor in modified metric (1) in powers of c^{-2}

$$\varphi = \sum_{k=0}^{\infty} \frac{1}{c^{2k}} \varphi^{2k} \quad (7)$$

with the solution of the nonrelativistic Schrödinger equation, φ^0 , and performing the nonrelativistic limit $c \rightarrow \infty$, one gets from eq. (5) a relation between large and small component, which holds

exactly for the Lévy-Leblond spinors (if g is chosen as a solution of the Schrödinger equation). Thus, for sufficiently large values of c —that is, small relativistic perturbation—functions of this type are suitable basis functions for solving the Dirac equation in modified metric (4) in its algebraic approximation: wave functions for which all expectation values are correct up to $O(c^{-2})$ can be expanded in such a basis set, and, for large values of c , the Dirac operator is bounded from below in the variational space. There is a one-to-one mapping between nonrelativistic (two-component) and relativistic (four-component) basis functions. Once the one- and two-particle matrix elements of the Dirac–Coulomb operator have been obtained, the calculation proceeds as in the nonrelativistic case. Because the basis set restricted to the Lévy-Leblond spinors can give a wave function only up to $O(c^{-2})$ this method cannot be used to calculate higher order relativistic corrections.

In the basis of the Lévy-Leblond spinors one gets for the matrix elements of the one-electron Dirac operator in c -dependent metric

$$D_{\mu\nu} = \langle \Psi'_\mu | \hat{D} | \Psi'_\nu \rangle = \langle g_\mu | \hat{T} + \hat{V} | g_\nu \rangle \cdot \langle \eta_\mu | \eta_\nu \rangle + \frac{1}{4c^2} \langle \phi_\mu | \vec{\sigma} \vec{p} \hat{V} \vec{\sigma} \vec{p} | \phi_\nu \rangle \quad (8)$$

where \hat{T} is the (nonrelativistic) kinetic energy operator, and for the metric

$$S_{\mu\nu} = \langle \Psi'_\mu | \Psi'_\nu \rangle = \langle g_\mu | g_\nu \rangle \cdot \langle \eta_\mu | \eta_\nu \rangle + \frac{1}{4c^2} \langle g_\mu | \hat{p}^2 | g_\nu \rangle \cdot \langle \eta_\mu | \eta_\nu \rangle \quad (9)$$

For choosing the electron interaction as

$$V(i, j) = \frac{1}{r_{12}}$$

thus describing the many-electron system by the Dirac–Coulomb Hamiltonian (the argumentation given here is not restricted to this special choice for the electron interaction and holds also for the Gaunt and Breit interaction) one gets, for the two-electron matrix elements in Mulliken notation

$$\begin{aligned} & (\Psi'_\mu \Psi'_\nu | \Psi'_\rho \Psi'_\sigma) \\ &= (\phi_\mu \phi_\nu | \phi_\rho \phi_\sigma) \\ &+ \frac{1}{4c^2} \left\{ \left(\vec{\sigma} \vec{p} \phi_\mu \vec{\sigma} \vec{p} \phi_\nu | \phi_\rho \phi_\sigma \right) \right. \\ &\left. + \left(\phi_\mu \phi_\nu | \vec{\sigma} \vec{p} \phi_\rho \vec{\sigma} \vec{p} \phi_\sigma \right) \right\} + O(c^{-4}) \quad (10) \end{aligned}$$

Inspection of the relativistic one- and two-electron matrix elements in the basis of Lévy-Leblond spinors shows a decomposition into a nonrelativistic part and a relativistic part with the leading order $O(c^{-2})$. Thus, the scalar first-order relativistic correction in the formulation of the DPT holds the same as for the quasi-relativistic Pauli operator. For both formulations, scalar first-order relativistic energy corrections can be obtained by using codes for analytical energy gradients where the integrals describing the nuclear displacement are replaced by the scalar relativistic parts of the integrals up to $O(c^{-2})$ given previously. This is the recipe given in a recent publication by Klopper.¹³

In the course of this work an extension of the MPGRAD program,¹⁵ which is part of the TURBOMOLE package,¹⁶ according to the following working equations

$$E_{\text{MP2DPT}} = \frac{1}{4c^2} \left\{ \sum_{rs} Y_{rs} \langle r | \vec{p} \hat{V} \vec{p} | s \rangle + \sum_{rs} W_{rs} \langle r | \hat{p}^2 | s \rangle + \sum_{rstu} \Gamma_{rstu} (rs | \vec{p} t \vec{p} u) \right\} \quad (11)$$

$$\begin{aligned} E_{\text{MP2MVD}} = \frac{1}{4c^2} & \left\{ \sum_{rs} Y_{rs} \left[2\pi \sum_A Z_A \langle r | \delta^3(\vec{r}_A) | s \rangle \right. \right. \\ & \left. \left. - \frac{1}{2} \langle r | \hat{p}^4 | s \rangle \right] \right. \\ & \left. - 2\pi \sum_{rstu} \Gamma_{rstu} \langle rs | \delta^3(\vec{r}_{12}) | tu \rangle \right\} \quad (12) \end{aligned}$$

and the corresponding equations for the calculation of the relativistic corrections of the SCF energy have been implemented.¹⁷ In eqs. (11) and (12), Y denotes the relaxed density matrix, W the energy-weighted density matrix, and Γ the relaxed two-particle density matrix, as known from the theory of MP2 gradients.^{18,19} Z_A is the nuclear charge of atom A . The MP2 results reported in this work were obtained from calculations in which all electrons were correlated. The relativistic density functional calculations were carried out with a code on top of the TURBOMOLE package,²⁰ which was augmented by a routine for the calculation of the two-electron Darwin term.²¹ The BP-86 functional^{22,23} was used throughout. For the velocity of light, a value of 137.0359895 a.u.²⁴ was used. Nuclei were considered point particles. The calculations have been carried out in part on IBM RS/6000

workstations in our laboratory and partly on the SGI PowerChallenge XL-12 of the Rechenzentrum der Ruhr-Universität Bochum.

Results and Discussion

Calculations for the scalar first-order relativistic correction to the MP2 energy by means of DPT, as well as perturbation theory based on the MVD operator, were performed for the ground state of the closed-shell atoms He, Be, Ne, and Ar. The energy data are presented in Table I. The calculations were carried out with basis sets used in the quoted references to make a direct comparison possible. From a methodological point of view, our calculations are essentially the same as those from ref. 13. They differ only in the manner of implementation. The results of ref. 13 were calculated by applying finite perturbation theory instead of using analytical gradients. Note that ref. 13 additionally contains relativistic corrections to MP3, MP4, CCSD, and CCSD(T) correlation energies. The results obtained in this work replicate those of ref. 13 in regard to all figures obtained. For the He and Be atoms, comparison with results from fully relativistic calculations (ref. 3) shows agreement within the limited accuracy (one digit) given in that work.

In the case of both the He and Be atoms, the DPT and MVD results differ only by a few hundredths of μE_h for the basis sets used. If one compares the MVD and DPT results from calculations with smaller basis sets, particularly for smaller sets of s-functions, the difference increases. For a basis set of TZP size, as typically used in quantum chemical calculations, the difference between them is 62 μE_h for the Ne atom. The difference between the TZP value and the result of a calculation with the considerably larger 14s10p8d6f basis amounts to 16 μE_h for DPT and 76 μE_h for MVD. This reflects the superior convergence behavior of the DPT compared to MVD approximation with respect to atom-centered Gaussian basis functions. This has already been found for one-electron systems.²⁵ As expected, the error of the approximate relativistic calculations increases with increasing value of the nuclear charge. Comparison with the DHF-MP2 values of refs. 26, 27, and 28 shows that the absolute error for DPT calculations is 8 μE_h for Ne and 84 μE_h for Ar, which correspond to a relative error of 3% for Ne and 8% for Ar.

The one- and two-electron contributions for the MVD correction to the MP2 energy are of the same order of magnitude but with different signs, which means that one should take two-electron Darwin

TABLE I.
MP2 Contributions to Scalar First-Order Relativistic Correction to Ground-State Energy of Selected Closed-Shell Atoms (Energies Given in μE_h).

| Atom | Basis | Method | One-electron contribution | Two-electron contribution | Relativistic correction | Reference |
|------|--------------------------|---------|---------------------------|---------------------------|-------------------------|--------------|
| He | 20s15p11d ³ | DTP | | | 1.67 | This work |
| | | MVD | − 10.466 | 12.122 | 1.66 | This work |
| | | DHF-MP2 | | | 2.0 | Ref. 3 |
| Be | 24s10p12d ³ | DPT | | | 8.05 | This work |
| | | MVD | − 56.967 | 64.982 | 8.01 | This work |
| | | DHF-MP2 | | | 8.0 | Ref. 3 |
| Ne | TZP ³⁰ | DPT | | | − 258.45 | This work |
| | | MVD | − 520.771 | 199.873 | − 320.90 | This work |
| | 14s10p8d6f ²⁶ | DPT | | | − 242.82 | This work |
| | | DPT | | | − 243.0 | Ref. 13 |
| | | MVD | − 803.430 | 558.655 | − 244.78 | This work |
| | | MVD | | | − 245.0 | Ref. 13 |
| Ar | 16s11p9d7f ²⁸ | DHF-MP2 | | | − 251.0 | Refs. 27, 28 |
| | | DPT | | | − 995.77 | This work |
| | | DPT | | | − 996.0 | Ref. 13 |
| | | MVD | − 3146.225 | 2144.883 | − 1001.34 | This work |
| | | MVD | | | − 1001.0 | Ref. 13 |
| | | DHF-MP2 | | | − 1080.0 | Ref. 28 |

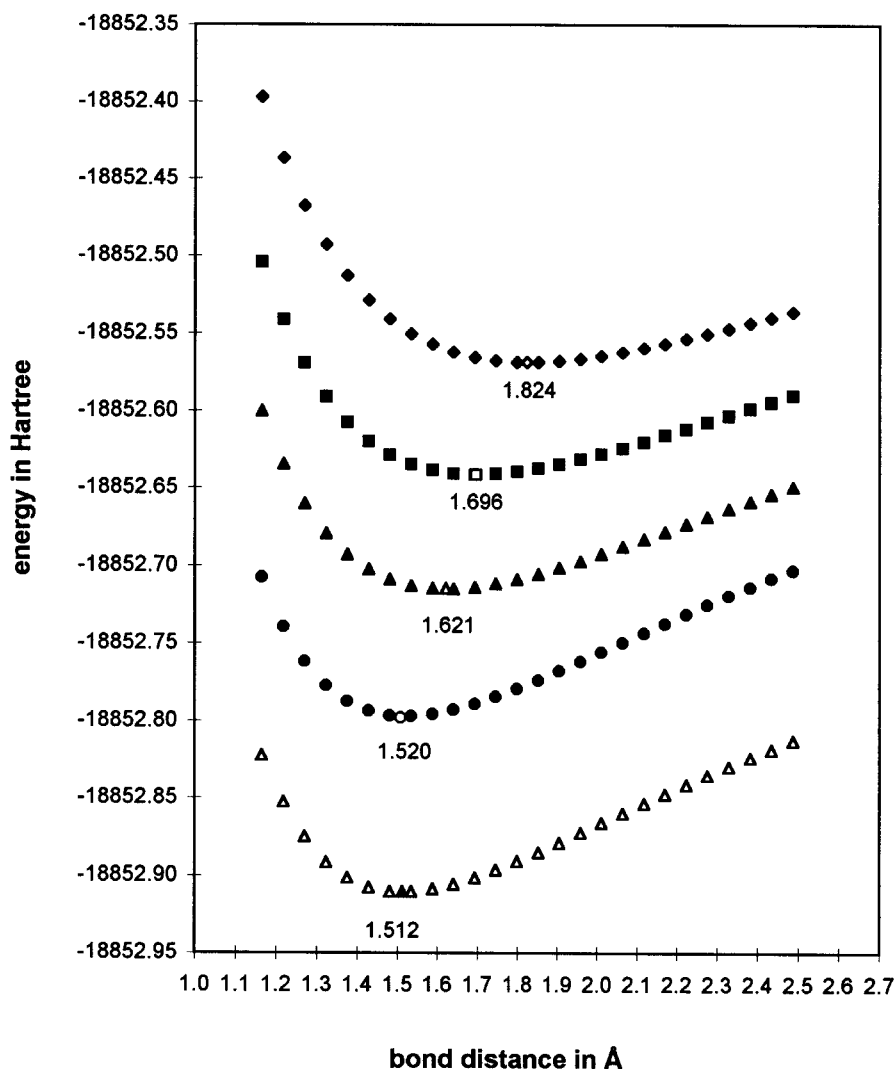


FIGURE 1. Potential energy curves of AuH. The SCF energies are shifted by -986.85 Hartree, the MP2 energies by -984.00 Hartree, and the SCF-DPT energies by -2.65 Hartree. The MP2-DPT (a) and MP2-DPT (b) values are plotted unchanged. The equilibrium distances are indicated by inverse colored plot symbols and given in angstrom units. (◆) SCF, (■) MP2, (▲) SCF-DPT, (●) MP2-DPT (a), (△) MP2-DPT (b).

term into account if one is interested in energy data calculated from the MVD perturbation. This is much less pertinent in the SCF case. For the Ne atom and the $14s10p8d6f$ basis set one gets a value of $-137331 \mu E_h$ for the one-electron contribution and $117 \mu E_h$ for the two-electron Darwin contribution at the Hartree-Fock level.

The coinage metal hydrides represent one of the most popular sets of molecules for investigating the different approximations in relativistic theory. We report on the study of bond lengths and harmonic frequencies within the DPT and MVD approximation employing MP2 as well as DFT with the BP-86 functional.^{22,23} The equilibrium distance

and the vibrational frequency have been obtained from a polynomial fit to a typical set of seven data points in the vicinity of the equilibrium distance. We compared our data mainly with DHF and DHF-MP2 results from a recent study by Collins et al.² For Cu, we used a $20s14p10d3f$ primitive basis set, starting from the $20s13p10d$ set of ref. 29, adding a p-set using the next exponent (s_{18}) from the well-tempered series, and adding three f-sets with exponents $s_{15}-s_{17}$ (for notation see ref. 29). This basis has been contracted to $15s10p7d3f$. For Ag, we started from the $23s16p13d$ basis set of ref. 29 and added a p-set (s_{21}) and five f-sets ($s_{17}-s_{21}$). The basis was then contracted to $18s13p10d5f$. For

Au, the 24s18p15d10f basis set of ref. 29 was augmented by one p-set (ζ_{22}) and contracted to 18s13p11d7f. For the hydrogen atom a standard TZP basis set³⁰ was employed.

The results for equilibrium bond distances and harmonic frequencies for CuH are presented in Table II. To investigate the effect of the two-electron Darwin term on molecular properties we additionally report results for the one-electron MVD perturbation denoted "1e." The E_{MP2DPT} and E_{MP2MVD} contributions incorporate the nonadditivity of relativistic and correlation effects, respectively. To examine the importance of this contribution, results are given for adding only the MP2 energy to the relativistic SCF results denoted by "(a)." Variant "(b)" also includes the cross-terms given by eqs. (11) and (12). The SCF and MP2 results of this work are in excellent agreement with the values of ref. 13. Comparison with the DHF values of ref. 2 shows that the nonrelativistic equilibrium distance on the Hartree–Fock level is reproduced perfectly, while there is a small deviation of 0.001 Å between DHF and SCF-DPT. The frequencies differ by 14 cm⁻¹ for the nonrelativis-

tic case and 10 cm⁻¹ for the relativistic calculations. On the MP2 level, the deviations are slightly larger. The bond length is 0.007 Å (0.005 Å) shorter, as the DHF-MP2 value from ref. 2 and the harmonic frequency 33 cm⁻¹ (57 cm⁻¹) larger for the nonrelativistic (relativistic) case. The main reasons for these deviations probably involve the use of different basis sets and the different treatment of core correlation in both studies. The DFT-DPT results show significantly larger differences from the DHF-MP2 results (0.019 Å [0.024 Å] longer and 84 cm⁻¹ [93 cm⁻¹] smaller in the nonrelativistic [relativistic case]), but match the experimental values better than those from the MP2-DPT or DHF-MP2 calculations. The results from MVD and DPT calculations are very similar for all methods. Inclusion of the two-electron Darwin term has almost no effect on bond lengths and harmonic frequencies.

The effect of the cross-term between relativity and correlation is small but significant. Neglect of this contribution leads to a 0.003-Å-longer bond length for both MVD and DPT and a smaller harmonic frequency (25 cm⁻¹ for DPT, 24 cm⁻¹ for MVD).

The results for AgH (Table III) show the same general behavior as those for CuH. The deviations between the DHF-MP2 values of ref. 2 and MP2-DPT, as well as MP2-MVD results, are similar to those in the case of CuH. Again, there is a greater difference between the full relativistic values from ref. 2 and the DFT results. The DFT values are remarkably close to the experimental data and very similar to the ZORA-DFT values of ref. 7. Neglect of E_{MP2DPT} or E_{MP2MVD} contributions leads to an increase in bond length of approximately 0.006 Å.

The relativistic and nonrelativistic potential energy curves of AuH are shown in Figure 1. Relativistic corrections are essential for the correct prediction of the molecular properties of AuH.

The relativistic contraction on the Hartree–Fock level of theory is 0.203 Å, calculated with first-order DPT. The corresponding value of ref. 2, calculated with DHF, is 0.261 Å. The contraction is significantly larger due to the importance of higher order relativistic contributions. The contraction effected by correlation determined on the MP2 level of theory calculated in this work is 0.128 Å. Collins et al. reported a value of 0.120 Å.² Assuming a simple additive relationship between the two, one would anticipate a combined relativistic and correlation contraction of 0.331 Å, based on the values in this work, and 0.381 Å using the data of ref. 2, but the

TABLE II.
Bond Lengths (r_e in Å) and Harmonic Frequencies (ω_e , in cm⁻¹) of CuH Calculated with a 20s14p10d3f Primitive Basis Contracted to 15s10p7d3f for Cu and a Standard TZP Basis for H Compared with Values from Literature.^a

| Method | Nonrelativistic | | Relativistic | |
|-----------------------|-----------------|------------|--------------|------------|
| | r_e | ω_e | r_e | ω_e |
| SCF-DPT | 1.569 | 1656 | 1.542 | 1709 |
| SCF-MVd1e | | | 1.542 | 1708 |
| SCF-MVD | | | 1.542 | 1709 |
| MP2-DPT (a) | 1.447 | 2057 | 1.426 | 2133 |
| MP2-DPT (b) | | | 1.423 | 2158 |
| MP2-MVD1e | | | 1.423 | 2157 |
| MP2-MVD (a) | | | 1.426 | 2134 |
| MP2-MVD (b) | | | 1.423 | 2158 |
| DFT-DPT | 1.473 | 1940 | 1.452 | 2008 |
| DFT-MVD1e | | | 1.453 | 2008 |
| DFT-MVD | | | 1.452 | 2009 |
| SCF-DPT ¹³ | 1.569 | | 1.542 | |
| MP2-DPT ¹³ | 1.450 | | 1.423 | |
| DHF ² | 1.569 | 1642 | 1.541 | 1699 |
| DHF-MP2 ² | 1.454 | 2024 | 1.428 | 2101 |
| Exp. ³³ | | | 1.463 | 1941 |

^a Variant (a) without the cross-term of (E_{MP2DPT} resp. E_{MP2MVD}) between relativity and correlation; variant (b) includes this term. "1e" denotes that the two-electron contribution is neglected.

TABLE III.
Bond Lengths (r_e in Å) and Harmonic Frequencies (ω_e in cm^{-1}) of AgH Calculated with a 23s17p13d5f Primitive Basis Contracted to 18s13p10d5f for Ag and a Standard TZP basis for H Compared with Values from Literature.^a

| Method | Nonrelativistic | | Relativistic | |
|-----------------------|-----------------|------------|--------------|------------|
| | r_e | ω_e | r_e | ω_e |
| SCF-DPT | 1.777 | 1490 | 1.706 | 1601 |
| SCF-MVD1e | | | 1.707 | 1600 |
| SCF-MVD | | | 1.706 | 1601 |
| MP2-DPT (a) | 1.651 | 1732 | 1.587 | 1883 |
| MP2-DPT (b) | | | 1.580 | 1907 |
| MP2-MVD1e | | | 1.581 | 1906 |
| MP2-MVD (a) | | | 1.586 | 1883 |
| MP2-MVD (b) | | | 1.580 | 1907 |
| DFT-DPT | 1.684 | 1615 | 1.619 | 1771 |
| DFT-MVD1e | | | 1.619 | 1770 |
| DFT-MVD | | | 1.619 | 1772 |
| DHF ² | 1.779 | 1473 | 1.700 | 1605 |
| DHF-MP2 ² | 1.663 | 1699 | 1.585 | 1873 |
| DFT-ZORA ⁷ | | | 1.62 | 1810 |
| Exp. ³⁴ | | | 1.618 | 1760 |

^a Variant (a) without the cross-term of (E_{MP2DPT} resp. E_{MP2MVD}) between relativity and correlation; variant (b) includes this term. “1e” denotes that the two-electron contribution is neglected.

difference between the MP2-DPT (b) value for the bond length and the value of the nonrelativistic SCF calculation is only 0.312 Å; that is, relativistic contraction at the MP2 level is much smaller. The corresponding value from ref. 2 is 0.334 Å. Inspection of Tables II and III shows that this distinctive nonadditivity is not present in the cases of CuH and AgH. A remarkable consequence of this study is that this nonadditivity *is not* connected to the cross-terms E_{MP2DPT} or E_{MP2MVD} —the difference between the MP2-DPT (a) value for the bond length and the value of the nonrelativistic SCF calculation is 0.304 Å. Adding independently the relativistic and correlation corrections to the Hartree–Fock potential energy curve yields bond length and vibrational frequencies not far different from the results of calculations including the cross-term. However, one may not, for example, simply add the relativistic and correlation bond contractions to evaluate the equilibrium distance starting from the Hartree–Fock value.

In comparison with the DHF-MP2 data, the relativistic equilibrium distance calculated with first-order MP2-DPT (b) is 0.018 Å too long and the DFT-DPT value 0.061 Å too long. The MP2-DPT

TABLE IV.
Bond Lengths (r_e in Å) and Harmonic Frequencies (ω_e in cm^{-1}) of AuH Calculated with a 24s18p15d10f Primitive Basis Contracted to 18s13p11d7f for Au and a Standard TZP Basis for H Compared with Values from Literature.^a

| Method | Nonrelativistic | | Relativistic | |
|--------------------------|-----------------|------------|--------------|------------|
| | r_e | ω_e | r_e | ω_e |
| SCF-DPT | 1.824 | 1499 | 1.621 | 1915 |
| SCF-MVD1e | | | 1.620 | 1911 |
| SCF-MVD | | | 1.620 | 1920 |
| MP2-DPT (a) | 1.696 | 1736 | 1.520 | 2284 |
| MP2-DPT (b) | | | 1.512 | 2321 |
| MP2-MVD1e | | | 1.511 | 2324 |
| MP2-MVD (a) | | | 1.519 | 2284 |
| MP2-MVD (b) | | | 1.510 | 2328 |
| DFT-DPT | 1.731 | 1622 | 1.558 | 2142 |
| DFT-MVD1e | | | 1.558 | 2146 |
| DFT-MVD | | | 1.557 | 2149 |
| DHF ² | 1.831 | 1464 | 1.570 | 2067 |
| DHF-MP2 ² | 1.711 | 1695 | 1.497 | 2496 |
| DKH-CCSD ³¹ | | | 1.525 | 2288 |
| DFT-ZORA ⁷ | | | 1.54 | 2290 |
| ARPP CEPA-1 ⁴ | | | 1.512 | 2254 |
| Exp. ³³ | | | 1.524 | 2305 |

^a Variant (a) without the cross-term of (E_{MP2DPT} resp. E_{MP2MVD}) between relativity and correlation; variant (b) includes this term. “1e” denotes that the two-electron contribution is neglected.

(b) value is in excellent agreement with the value of Schwerdtfeger et al.⁴ calculated with a relativistic pseudopotential and the CEPA-1 approximation. Concerning the DKH-CCSD approach, which gives the best theoretical prediction of properties for AuH documented so far,³¹ the deviation of the MP2-DPT (b) value is 0.013 Å for the equilibrium distance and 33 cm^{-1} for the harmonic frequency. Although the quality of the MP2 and DFT results are certainly comparable (MP2 bond lengths are slightly too small, DFT bond lengths too long), one must remember that the DFT calculations are at least one order of magnitude less demanding.

Conclusions and Outlook

It has been shown that the decomposition of the matrix elements of the DPT approach into a non-relativistic part and a relativistic perturbation follows from a matrix representation in a basis of Lévy-Leblond spinors. The first implementation for the calculation of relativistic corrections to the

MP2 energy by means of DPT and MVD with a MP2 gradient program has been described. Comparison with relativistic DFT calculations and literature data indicates the reliability of this method. It seems to be very promising to implement this ansatz into an RI-MP2 gradient program such as the one most recently developed by Weigend and Häser.³²

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